

The Canadian Mineralogist
Vol. 50, pp. 667-674 (2012)
DOI: 10.3749/canmin.50.3.667

ENIGMATIC X-RAY MAGNETIC CIRCULAR DICHROISM IN GREIGITE (Fe₃S₄)

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ABSTRACT

Greigite (Fe₃S₄), a widely occurring iron thiospinel, was investigated using soft X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). XAS and XMCD spectra were recorded at the Fe *L*_{2,3} edges for pure synthetic and natural greigite samples. At the Fe *L*₃ edge, the XAS spectra reveal two main absorption peaks at 707.2 and 708.6 eV, which are interpreted to originate from greigite and an oxidized surface layer on greigite crystals. The XMCD spectra, which are dominated by a greigite signal, contain three peaks at 705.3, 706.2, and 707.7 eV, all with the same sign. The expectation is that the spectrum would have two negative peaks representing Fe²⁺ and Fe³⁺ in octahedral coordination, and a positive peak representing Fe³⁺ in tetrahedral coordination, as found in stoichiometric magnetite (Fe₃O₄). A reasonable fit of the XMCD data can be achieved without the tetrahedral Fe component, which contradicts magnetic structural information provided by neutron diffraction analysis, and uses unreasonable parameters. The conundrum between theory and experimental data may be caused by the strong covalent effect in sulfides, which causes broadening of the hybridized XMCD peaks and also indicates that multiplet calculations cannot fully predict the properties of greigite. Our results indicate covalent 3*d* states in greigite, which can destroy the half-metallicity that is present in magnetite. Our measurements represent the best available XAS and XMCD spectra for greigite, but further experimental and modeling information are needed to explain the observed XMCD spectra and to understand what it represents in terms of electronic and magnetic structure. This is important because greigite widely contributes to the magnetic properties of sedimentary rocks.

Keywords: greigite, XMCD, XAS, electronic structure, magnetism

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INTRODUCTION

Greigite (Fe_3S_4) is an iron thiospinel (where oxygen is replaced by sulfur) mineral that shares a similar crystallographic and magnetic structure (e.g., Skinner *et al.* 1964, Coey *et al.* 1970, Chang *et al.* 2009a) with magnetite (Fe_3O_4), where the difference in covalence of iron with sulfur and oxygen leads to different properties (e.g., Spender *et al.* 1972, Roberts 1995, Dekkers & Schoonen 1996, Chang *et al.* 2008, Roberts *et al.* 2011). Greigite has been widely identified in natural environments. It commonly forms in sulfate-reducing diagenetic sedimentary environments, hydrothermal ore deposits, and other hydrothermal environments. It is a strongly magnetic mineral that is often the main carrier of paleomagnetic and paleoenvironmental information through remanent magnetization and environmental magnetic proxies in such settings (e.g., Roberts *et al.* 2011). Greigite also forms as a biomineral that is produced by a range of organisms, such as magnetotactic bacteria (e.g., Konhauser 1998, Bazylinski & Frankel 2004) and a gastropod found in deep-sea hydrothermal vents (Warén *et al.* 2003).

Band structure calculations suggest that greigite is a semi-metal (Devey *et al.* 2009), although spin-resolved experiments would be required to confirm this interpretation. This may place greigite within a select group of materials with potential spintronics applications (cf. Wolf *et al.* 2001). Another recent electronic structure calculation indicates that greigite is a normal metal, in contrast to halfmetallic magnetite (Zhang *et al.* in press). They found that the existence of sheets of the Fermi surface depends on the direction of the magnetization in greigite, which could enable spinorbitronics. Despite the widespread terrestrial occurrence and importance of greigite, its mineralogical properties are relatively poorly constrained. Pure synthetic greigite has only recently been produced in the laboratory (Tang *et al.* 2007, Chang *et al.* 2008). The synthetic greigite samples have been used to determine the fundamental structural and magnetic properties of greigite (Chang *et al.* 2008, 2009a). Neutron diffraction and Rietveld profile analysis of these samples indicate a collinear ferrimagnetic structure of greigite with lower spin moments for iron compared to studies of magnetite (Chang *et al.* 2009a). This firmly established its crystallographic and magnetic structures. However, its electronic structure (i.e., valence and electron correlation) is less well understood, and details of the site distribution of Fe^{2+} and Fe^{3+} ions in greigite are not defined. Neutrons can only probe the average magnetic moments of Fe ions in the crystal lattice. Synchrotron-based X-ray spectroscopic techniques can provide quantitative information for cation site occupations in ferri- and ferromagnetic minerals and have been used successfully for magnetite (Patrick *et al.* 2002, Morrall *et al.* 2003), natural ferrite spinels (Patrick *et al.* 2002, Pearce *et al.*

2006), and bio-spinels (Coker *et al.* 2007, 2008). We report X-ray absorption spectroscopic (XAS) and X-ray magnetic circular dichroism (XMCD) measurements for pure greigite samples to investigate its electronic and magnetic structure.

SAMPLES

The pure synthetic greigite samples used for the synchrotron experiments are the same as those used for previous neutron scattering experiments (Chang *et al.* 2009a). They were prepared by hydrothermally reacting ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) with thiourea ($\text{CH}_4\text{N}_2\text{S}$) and formic acid (HCOOH) at 170 °C for eight hours (Tang *et al.* 2007, Chang *et al.* 2008). The samples have been confirmed to be single-phase greigite that occurs as large polycrystalline grains (in the 10 μm diameter range) (Chang *et al.* 2008). After synthesis, the greigite samples were placed in small glass sample containers and stored in a desiccator to prevent wet oxidation. Measurements were also made for the purest natural greigite samples in our collection from Italy (Florindo & Sagnotti 1995, van Dongen *et al.* 2007) and Taiwan (Jiang *et al.* 2001). Greigite is the only magnetic phase in these natural greigite samples. The greigite concentration by mass exceeds 30% as inferred from their saturation magnetization values. The impurities mainly consist of paramagnetic pyrite (FeS_2) and organic material. Detailed information about the studied greigite samples is provided by Chang *et al.* (2008, 2009a,b).

METHODS

In X-ray absorption, core electrons are excited into an empty $3d$ state above the Fermi level and thus XAS provides element specific information about the coordination environment of the atoms and their electronic state. XMCD is the difference spectrum of two X-ray absorption spectra taken with opposite magnetic fields and measured with circularly polarized X-rays. The resulting Fe $L_{2,3}$ XMCD spectra provide information about the local electronic structure of the absorbing atom through excitation of $2p$ core electrons by electric-dipole transitions into localized unoccupied $3d$ states (van der Laan & Thole 1991). XMCD is a unique element- and site-specific probe of the magnetism for ferri- and ferromagnetic minerals (Patrick *et al.* 2002, Pearce *et al.* 2006).

XAS and XMCD spectra were measured at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory, California, USA. The pure synthetic and natural greigite samples were ground in an anaerobic cabinet and mounted onto conducting carbon tape attached onto a copper sample holder. Surficially oxidized material was cut from the natural greigite-bearing sedimentary rocks prior to sample grinding and mounting. Samples were maintained in

an anaerobic environment during sample loading into the vacuum chamber, using a specially designed holder, to avoid oxidation of newly exposed mineral surfaces after grinding.

The measurements were made at the magnetic spectroscopy beamline 4.0.2, where the X-ray beam is monochromatized by a variable-included-angle plane-grating monochromator, resulting in an instrumental energy resolution of ~ 0.1 eV. The incident and absorbed photon flux were monitored in total-electron-yield (TEY) mode. XAS spectra were acquired with circularly polarized photons in an applied magnetic field of ± 0.6 T, which was reversed at every energy point, providing two polarized XAS spectra. The direction of the X-ray beam is along the magnetization direction. The two polarized XAS spectra were normalized to the incident beam intensity and their difference gives the XMCD (Patrick *et al.* 2002, Pearce *et al.* 2006).

The calculated XMCD curves for each Fe site used in the fitting were first convoluted using a Gaussian line shape to account for instrumental peak broadening. In these atomic multiplet calculations (van der Laan & Thole 1991, van der Laan 2006), the Hartree-Fock Slater integrals for the $3d$ - $3d$ and $2p$ - $3d$ Coulomb and exchange interactions were scaled to 70% and 80%, respectively. The calculated XMCD spectra were fitted to the L_3 edge peaks, which have been shown to give meaningful results (Patrick *et al.* 2002).

RESULTS

XAS and XMCD spectra for a synthetic and a natural greigite sample are shown in Figure 1. The XAS spectra contain two main absorption peaks at 707.2 and 708.6 eV at the Fe L_3 edge, when calibrated to the main XAS peak for magnetite at 708.8 eV (after Regan *et al.* 2001) (Fig. 1a). Comparison of a representative greigite XAS spectrum with those for magnetite ($\text{Fe}^{2+}:\text{Fe}^{3+} = 1:2$) and goethite (all Fe^{3+}) reveals that the main XAS peak in greigite is shifted to lower energies ~ 0.2 eV (Fig. 2a). In addition, the shape of the peak differs from that of the mixed Fe valence in magnetite and that of the Fe^{3+} -bearing phase in goethite in that it has a far greater intensity on the lower energy side of the L_3 edge at 707.2 eV (Fig. 2a). XMCD spectra derived from the greigite samples have three negative peaks at energies of 705.3, 706.2, and 707.7 eV (Fig. 1b), which contrasts with the XMCD spectra obtained for a standard natural magnetite (Fig. 2b) (Patrick *et al.* 2002, Pearce *et al.* 2006, Coker *et al.* 2007). In magnetite, the three distinct peaks in the XMCD spectrum correspond to the three main coordination environments of Fe, namely (with increasing energy), negative octahedral (O_h) Fe^{2+} , positive tetrahedral (T_d) Fe^{3+} , and negative O_h Fe^{3+} peaks (Fig. 2b). These peaks are not all seen in the greigite XMCD spectra where the positive component (representing T_d Fe^{3+} in magnetite) is absent (Fig. 2b).

DISCUSSION

The two main peaks in the Fe L_3 edge XMCD spectrum for greigite are at 706.2 and 707.7 eV, with an energy separation of 1.5 eV (Fig. 1b). These two XMCD peaks do not coincide with the main intensity peaks in the XAS spectra (at 707.2 and 708.6 eV) (Fig. 1a). Instead, the main negative peaks of the XMCD spectrum coincide with the trough between the two main XAS peaks (Fig. 1; the vertical dotted line is a guide). This indicates that the high-energy component of the XAS spectra is non-magnetic (paramagnetic or antiferromagnetic), which is consistent with the presence of an oxidized Fe-species, such as goethite (Fig. 2a). Although the samples were mounted anaerobically, the crystals were in air prior to that. New surfaces of greigite, exposed during anaerobic grinding, will not have been oxidized, but outer surfaces of the individual synthetic greigite crystals and the natural crystals had plenty of opportunity to interact with O_2 . Thus, the non-magnetic species is likely to be an oxidized surficial ('outer') layer on the greigite crystals. The signal of the Fe $L_{2,3}$ XAS in TEY mode decreases exponentially with a probing depth of ~ 5 nm, so that the spectrum is dominated by the outer layers of the sample. An oxidized layer has been observed surrounding greigite grains using transmission electron microscopy (TEM) in electron energy loss spectroscopy (EELS) by Letard *et al.* (2005) and Kasama *et al.* (2006). In these studies, a thin amorphous oxidized surface layer (a few nm) was often observed. The shape of the XAS spectra presented here is similar to that reported for greigite by Letard *et al.* (2005), who attributed the surficial layer to an amorphous oxide with composition close to ferrihydrite or hematite ($\alpha\text{-Fe}_2\text{O}_3$). However, Letard *et al.* (2005) found that the maxima of the two XMCD peaks occur at the same energies as the XAS maxima for their greigite samples. This suggests that in their greigite samples, the surficial oxide is partially magnetic (e.g., $\gamma\text{-Fe}_2\text{O}_3$), but this requires further investigation. In another brief laboratory report, Hitchcock *et al.* (2010) presented novel XAS and XMCD spectra recorded from individual greigite magnetosome crystals using scanning transmission X-ray microscopy. Although no clear XMCD signature for greigite could be extracted, their XAS spectra are different from our results in that they observed two peaks at ~ 708.5 and 710 eV with a relatively larger intensity of the lower peak. They attribute this to a more reduced nature of their bacterial samples. It should be noted that the substantial peak at lower energy in the goethite XAS spectrum is consistent with calculated spectra (van der Laan & Kirkman 1992) for O_h Fe^{3+} (d^5), which contain two peaks with an energy separation of ~ 1.5 eV. In the greigite XAS spectra, the peak at lower energy is at roughly the same position as would be expected for O_h Fe^{2+} (d^6). Therefore, this peak at lower energy probably contains both

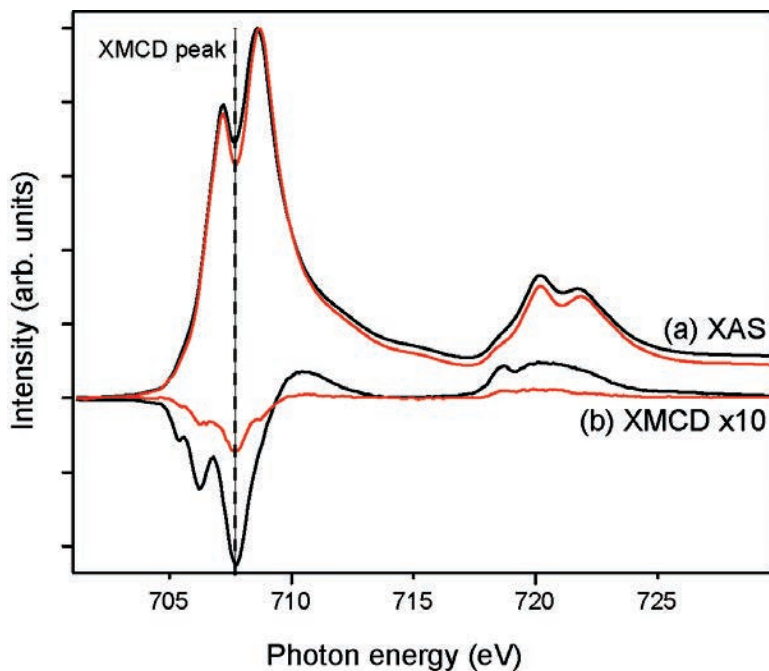


FIG. 1. Fe $L_{2,3}$ XAS and XMCD spectra for greigite. (a) XAS spectra and (b) corresponding XMCD spectra for synthetic (black) and natural (red) greigite. The XAS spectra were normalized to their maximum peak. The noticeable intensity difference in the corresponding XMCD patterns is because the natural greigite samples contain non-magnetic iron-bearing materials, such as pyrite and clay minerals, which contribute to the XAS, but not to the XMCD signal. The dotted line indicates that the strong negative XMCD peak is derived from the trough between the two main XAS peaks, rather than from the high-energy XAS maxima.

Fe^{3+} and Fe^{2+} . In covalent compounds, the position of this lower energy Fe^{3+} peak might be shifted, e.g., by the Madelung potential, as seen in FeS_2 where the $\text{Fe } L_3$ XAS spectrum has a somewhat lower energy than in magnetite (Thole & van der Laan 1988). The Madelung potential is the electrostatic potential of a single ion in a crystal by approximating the ions by effective point charges. The effective point charges and distances of oxygen in magnetite and sulfur in greigite are different and hence change the electrostatic potential, which shifts the energies of the absorption peaks. This helps to explain some of the observed shift in energies in the XAS spectra.

Apart from a decreased signal, the measured XMCD spectrum is not affected by the non-magnetic oxide layer: it therefore originates from the ferrimagnetic greigite, or from the interface with the surficial oxide layer. However, the observed XMCD spectrum is significantly different from that expected for a ferrimagnetic inverse spinel (e.g., Patrick *et al.* 2002), and the contrast with the spectrum for magnetite is striking (Fig. 2b). Neutron diffraction and Mössbauer analyses

for greigite (e.g., Coey *et al.* 1970, Spender *et al.* 1972, Chang *et al.* 2008, 2009a) indicate that it has a collinear ferrimagnetic structure similar to that of magnetite. Therefore, the XMCD spectra would be expected to have the same $O_h \text{Fe}^{2+}$, $O_h \text{Fe}^{3+}$, and $T_d \text{Fe}^{3+}$ components observed in stoichiometric magnetite (e.g., Patrick *et al.* 2002, Morrall *et al.* 2003, Pearce *et al.* 2006, Coker *et al.* 2007, Carvallo *et al.* 2008) (Fig. 2b). Calculations of the expected XMCD contributions for the three Fe sites in greigite (Fig. 3a) indicate that the maxima in the XMCD spectra are coincident with the maxima of the XAS spectra. Iron in greigite has a fairly high spin and, given the larger crystal field in sulfides compared to oxides (Burns 1993), the crystal field values used for the sites were chosen as $d^5 O_h = 2.5$ eV, $d^5 T_d = 1.1$ eV, and $d^6 O_h = 1.6$ eV; larger values would result in low-spin configurations. Using these values to fit the measured data, a reasonable agreement between the calculation and the experiment is obtained by including only the $d^5 O_h$ and $d^6 O_h$ peaks while omitting the $d^5 T_d$ one (Fig. 3b). Letard *et al.* (2005) produced a similar greigite spectrum to that seen here (but at a different energy

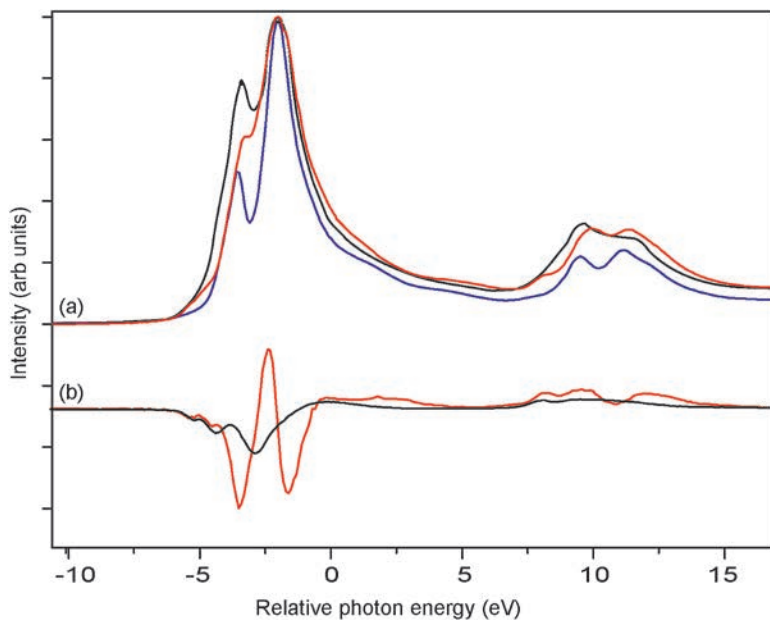


FIG. 2. Comparison of XAS and XMCD spectra for greigite, magnetite and goethite. (a) Fe $L_{2,3}$ XAS and (b) corresponding XMCD spectra for synthetic greigite (black) and natural magnetite (red) (Pearce *et al.* 2006) compared to a goethite (blue) XAS spectrum. The XAS spectra were normalized to their maximum peak.

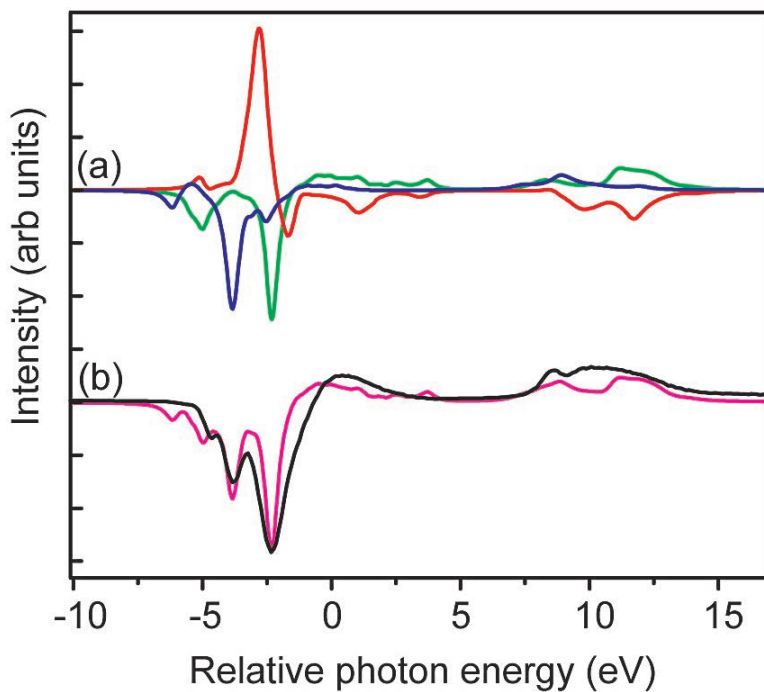


FIG. 3. Comparison of calculated and measured XMCD spectra for greigite. (a) Calculated spectra for O_h Fe^{2+} (blue), T_d Fe^{3+} (red), and O_h Fe^{3+} (green). (b) Experimental XMCD spectra for synthetic greigite (black) compared to the sum of the calculations from (a) for O_h Fe^{2+} and O_h Fe^{3+} (magenta).

position with respect to the XAS) and suggested that the difference in the XMCD spectra between greigite and magnetite is attributable to the possible presence of Fe vacancies in greigite, similar to the case for maghemite ($\gamma\text{-Fe}_2\text{O}_3$). However, this contradicts the neutron diffraction study on greigite. Rietveld profile analysis of the neutron diffraction pattern, which included parameters for partial occupancy of the Fe sites, indicates that the greigite samples studied here do not have a significant vacancy concentration (Chang *et al.* 2009a). Similarly, Qian *et al.* (1999) determined the composition of their hydrothermal synthetic greigite and found that the greigite samples are nearly stoichiometric ($\text{Fe}_{2.994}\text{S}_4$).

If the measured XAS spectra (Fig. 1a) contain contributions from Fe_3S_4 and Fe-oxide, the XMCD results may also be explained if the spectrum is derived from mainly $O_h\text{Fe}^{2+}$ and the $T_d\text{Fe}^{3+}$ and $O_h\text{Fe}^{3+}$ signals largely cancel each other. The $T_d\text{Fe}^{3+}$ and $O_h\text{Fe}^{3+}$ peaks can be at the same energy position, and if they have the same but opposite magnetic moment the high-energy part of the XMCD spectrum disappears. This explanation would account for the magnetic moments at all three different sites, but fitting the measured XMCD spectrum by summing the three individual calculated spectra does not give a convincing comparison with experiments (Fig. 3b). Part of the problem is that the strong covalent sulfur bindings complicate the XMCD properties of greigite. A relatively high degree of covalency in sulfides compared to oxides of similar structure is well known (*e.g.*, Coey *et al.* 1970, Spender *et al.* 1972, Devey *et al.* 2009), which is also supported by the measured lower saturation magnetization for greigite ($3.13\ \mu_B/\text{formula unit}$ at room temperature) compared to magnetite (Chang *et al.* 2008). Neutron powder diffraction results also indicate lower magnetic moments of iron (both Fe^{2+} and Fe^{3+} in the two sublattices) in greigite (Chang *et al.* 2009a). For example, the magnetic moments of the iron in the three different sites of Fe_3S_4 are $+2.99\ \mu_B$, $-3.17\ \mu_B$, and $-3.17\ \mu_B$, which gives a net moment of $3.35\ \mu_B$ at 100 K (Chang *et al.* 2009a). Compared to Fe_3O_4 at 130 K, the magnetic moments are $+4.20\ \mu_B$, $-3.97\ \mu_B$, and $-3.97\ \mu_B$, which gives a net moment of $3.74\ \mu_B$ (Wright *et al.* 2002). The strong covalent sulfur bindings in greigite mean that it cannot be well constrained using multiplet calculations and that the hybridized peaks might also be broadened in some way. Our results show covalent 3d states in greigite. This covalency can possibly destroy the half-metallicity that is present in magnetite. More XAS and XMCD experiments and theoretical modeling are needed to constrain the electronic structure of greigite.

CONCLUSIONS

The XAS spectra at the Fe L_3 edge for synthetic and natural greigite samples have two absorption peaks at 707.2 and 708.6 eV, which are probably due to absorptions from greigite and the thin oxidized layer

surrounding the greigite crystals. The low- and high-energy XAS peaks are interpreted to represent dominant absorption from Fe^{2+} and Fe^{3+} in greigite and oxide Fe-species in the shell of greigite grains, respectively. The XMCD spectra, which should represent a dominant greigite signal, have three negative peaks at 705.3, 706.2, and 707.7 eV. This is not expected, considering its ferrimagnetic structure, and is also significantly different from that of stoichiometric magnetite. A reasonable XMCD fit can be achieved without the $T_d\text{Fe}^{3+}$ component. However, this is not consistent with neutron diffraction results from the same greigite samples, which indicate an almost full site occupation of Fe in greigite. This discrepancy may be caused by the strong covalent sulfur binding in greigite, which means that multiplet calculations cannot be well performed for greigite and that the hybridized XMCD peaks may also be broader. Nevertheless, our results represent the best available XAS and XMCD spectra for greigite and provide valuable information on the poorly constrained mineralogical behavior of this increasingly important magnetic mineral.

ACKNOWLEDGEMENTS

We thank the Advanced Light Source (ALS) for access to beamline 4.0.2. The ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We are grateful to beamline scientist Elke Arenholz for technical assistance and to Carolyn Pearce and Neil Telling for their assistance with measurements. We are grateful to two anonymous reviewers and the Associate Editor Yuanming Pan for comments that improved this paper. We thank Editor Lee Groat for editorial handling. This work contributes to the objectives of NERC grant NE/G003319/1 to APR and an EPSRC grant awarded to RP and VC.

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Received January 24, 2012, revised manuscript accepted June 25, 2012.